ESTERS AS REPELLENTS*

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Abstract

House flies (*Musca domestica*) and several blood sucking Diptera are repelled by unsaturated cyclic esters, including certain substances which are without odor to man. Acetates of terpine alcohols are in every case superior to the corresponding alcohols.

In 1927, while employed on a Crop Protection Institute Fellowship supported by Stanco Incorporated, I undertook to develop an "odorless repellent," that is, to discover a substance which would repel insects, but whose odor would not be detectable by man. It was proposed to learn what kinds of chemicals would repel insects as a guide to selecting odorless substances for field testing.

In the early stages of this study I was fortunate in having access to a large mass of unpublished data accumulated by Mr. F. C. Nelson, formerly of this station and at present Biologist for Stanco Incorporated. Nelson's methods were such that the comparative efficiency of the substance tested was clearly shown. Having treated various parts of his body with the materials to be compared, he exposed himself to mosquitoes and compared the length of time each treatment remained effective.

Nelson tested a large number of essential oils, terpenes and esters. I was able to acquaint myself with the composition of many of them by consulting reference books on the subject. I then attempted to correlate the chemical nature of the repellents with their relative effectiveness as recorded by Nelson, and certain correlations were discovered. It was found that terpene alcohols as a class were superior to terpene hydrocarbons. Nelson had tested linalyl acetate and oil of lavender which contains linalool; geranyl acetate and the oils of rose geranium and citronella, both containing geraneol; terpinyl acetate and ter-

* Paper of the Journal Series, New Jersey Agricultural Experiment Station, Department of Entomology.

pineol. In each instance the ester had proved superior to the corresponding alcohol. This suggested that repellent efficiency increases from hydrocarbon to alcohol to ester. Some of my work on repellents was arranged so that this hypothesis could be tested.

The materials studied were tested by comparing the relative length of time equal volumes on equal surfaces continued to repel flies. The surfaces used were filter papers wet with molasses and water. After treatment the papers were exposed at the college dairy and the behavior of the flies closely observed.

The reaction of the flies was very definite when they were numerous and hungry. At other times it was difficult to make comparisons because of the scarcity of flies or their indifference to the molasses. Observations were recorded in terms of the number of flies feeding on each paper after various time intervals. There were other indications which were significant to the observer but which are difficult to record. If flies fed on the molasses the filter paper became much whiter. A single fly feeding at the same spot for any length of time would often leave a small white area free from molasses as an indication of its visit. In the case of some materials, flies would, from time to time, "take a taste" and leave immediately. By taking such indications into consideration the observer was usually able to distinguish differences among the materials, provided a reasonable number of hungry flies were present. The differences were often much more marked than is indicated by the numerical data.

In the case of the poorer repellents, comparisons were most striking when pure materials were used. In testing the better repellents, dilution was desirable so that differences would become apparent more quickly.

A series of comparisons consisted of papers which were prepared and treated at the same time, in the same way and with the same volume of repellent liquid and which were exposed at the same time and place. Each such series will be tabulated separately. Within a series comparisons are shown between the materials tested. Materials which are not compared in one series may be compared in another, or their relative value may

TABLE I

COMPARATIVE REPELLENT EFFICIENCY OF CERTAIN MIXTURES, SHOWING NUMBER OF FLIES FEEDING WHEN OBSERVATIONS WERE TAKEN

Mixtures	P.M. 8/13		A.M. 8/14				P.M. 8/14				Order of efficiency
	4:30	5:00	9:00	10:00	11:00	12:00	1:00	1:30	2:00	2:30	
Containing menthol	0	0	1	0	1	2	2	1	5	6	5
Containing eugenol	0	0	0	1	0	1	0	3	3	2	4
Containing cedarwood	0	0	3	1	4	5	10	1	4	4	5
Check	1	1	0	0	1	2	4	7	5	9	
Containing sandalwood	0	0	0	0	0	0	0	5	1	3	2
Check	9	4	1	1	5	7	9	3	8	11	
Check	9	9	4	4	8	15	18	10	10	13	
Containing eugenol acetate	0	0	0	0	0	1	3	5	4	5	3
Containing pinene HCl	0	0	1	0	1	3	7	7	10	6	5
Containing menthyl acetate	0	0	0	0	0	1	2	1	–	2	3
Containing santalyl acetate	0	0	0	0	0	0	0	0	0	0	1
Check	13	9	2	0	4	5	4	4	4	4	

be inferred from their differences from another material with which both have been compared.

Series 1

August 13. 2.5 c.c. of liquid repellents or 2.5 gm. of solids were dissolved in 97.5 c.c. of kerosene-pyrethrum and the mixtures compared with each other, with Flit and with kerosene-pyrethrum. They were exposed at 4:30 P.M. on the 13th and examined at intervals until 2:30 P.M. on the 14th. The observations are given in table I.

The testing was resumed about the middle of September. At this season the flies did not react as strongly as in August. In order to bring out difference between different materials it was necessary in many cases to use the pure repellents without dilution.

In Series 2 undiluted materials were used. The observations follow in table II.

At 5:30 P. M. September 14th the behavior of the flies indicated that terpineol and cedarwood had lost all repellent properties.

At 11:00 A. M. September 15th santalol, santalyl acetate and terpinyl acetate still retained their repellent properties. Continued observations determined that the disc treated with santalyl acetate remained repellent the longest.

In Series 3 undiluted repellents were compared with yprethrum extracts. The observations follow in table III.

The figures do not show any difference between santalyl acetate and terpinyl acetate and do exhibit considerable differences among different trials of the same materials. This irregularity was due to the difficulty of covering the discs uniformly with the repellent. A definite end point would be reached when flies fed on all portions of the disc. This occurred with menthyl acetate at 5:30. It did not occur with terpinyl acetate, santalyl acetate or the kerosene pyrethrum combinations in three days. On the third day, however, a marked superiority of the santalyl acetate and the pyrethrum concentrate was apparent to the observer. The materials tested are, therefore, ranked as follows:

1. Pyrethrum concentrate: santalyl acetate.

TABLE II

COMPARISONS OF CERTAIN REPELLENTS

Repellent	P.M. 9/14		2:00	2:30	2:45	3:00	3:30	4:00	5:15	6:00	7:00	A.M. 9/15	Order of efficiency
	1:30	1:45										11:00	
Terpineol	0	0	1	1	1	5	2	1	1	2	1	4	5
Check	5	2	4	10+	3	4	5	9	7	9	8	2	
Cedarwood	2	0	0	4	0	3	2	6	6	1	3	3	6
Check	3	1	2	7	5	3	9	7	10+	5	5	4	
Santalyl acetate	0	0	0	0	0	0	0	0	0	0	0	0	1
Santalol	0	0	0	0	0	0	0	0	0	0	0	0	2
Check	0	3	8	12	5	8	7	9	8	10+	7	4	
Terpinyl acetate	0	1	0	0	0	0	1	0	0	0	0	0	3
Deodorized kerosene-pyrethrum	1	0	0	0	1	2	1	1	0	4	3	1	4

TABLE III

THE DISCS WERE EXPOSED AT NOON SEPTEMBER 15 AND OBSERVED AT INTERVALS UNTIL 5:15 P. M.

Repellents	1:30	1:45	2:00	2:30	2:45	3:00	3:30	4:00	5:15	Total Flies
Terpinyl acetate	0	0	0	0	1	0	1	0	0	2
" "	0	0	0	1	0	1	1	2	1	6
" "	0	1	0	2	6	1	3	2	1	16
Santalyl acetate	0	0	2	0	3	1	2	0	0	8
Check	0	0	3	10	7	10	5	10	4	49
Menthyl acetate	1	1	0	0	0	0	4	1	1	8
Santalyl acetate	1	0	0	0	0	0	1	1	1	4
Check	1	6	3	7	3	6	4	7	1	38
Deoderized kerosene	1	0	1	7	6	6	5	10	5	41
Check	2	1	3	4	3	6	4	4	10	37
Kerosene-pyrethrum con.	0	1	0	0	0	0	1	2	0	4
Deoderized kerosene and pyrethrum	0	1	1	1	0	0	0	2	2	7

2. Pyrethrum (dilute) in deodorized kerosene: terpinyl acetate.
3. Menthyl acetate.
4. Deodorized kerosene (worthless).

Series 4

This was a repetition of series 3 and led to the same conclusions. Pyrethrum concentrate and santalyl acetate were carefully compared. It was observed that the former remained partially repellent for the longer time; while the latter repelled *all* flies for the longer time.

In Series 5–10 essential oils of unknown or doubtful composition were compared with terpinyl acetate, santalyl acetate and santalol and none were found to equal them. Acetylization was found to increase the efficiency of oil of Java citronella and of oil of spruce.

The terpenes, their alcohols and acetates may now be compared by arranging them in the order of excellence found in the first three series of comparisons. The arrangement follows:

Series 1

(1) Santalyl acetate
(2) Santalol
(3) { Eugenol acetate
     Menthyl acetate
(4) Eugenol
(5) { Pinene HCl
     Oil cedarwood
     Menthol

Series 2

(1) Santalyl acetate
(2) Santalol
(3) Terpinyl acetate
(4) Terpineol
(5) Oil cedarwood

Series 3

(1) Santalyl acetate
(2) Terpinyl acetate
(3) Menthyl acetate

Combining the three series the order of excellence of all the materials is about as follows:

Order	*Chemical classification*
(1) Santalyl acetate	ester, sesquiterpene
(2) Santalol	alcohol, sesquiterpene
(3) Terpinyl acetate	ester, terpene
(4) Eugenol acetate	ester, phenol
(4) Menthyl acetate	ester, terpene, saturated
(5) Eugenol	alcohol, phenol
(5) Terpineol	alcohol, terpene
(6) Menthol	alcohol, terpene, saturated
(6) Pinene HCl	terpene, saturated
(6) Oil cedarwood	hydrocarbon, sesquiterpene

It will be seen that (1) all esters are better than the corresponding alcohols, (2) the saturated alcohol, menthol, is inferior to the unsaturated alcohols, (3) the hydrocarbon, oil of cedarwood is inferior to all alcohols except menthol, (4) the best material is a very slightly volatile unsaturated, cyclic ester.

Further, extensive field and laboratory experiments with cyclic esters brought out the superior repellent properties of the dialkyl phthalats (U. S. Patent ♯1,727,305) and of the pyrethrins to other substances. Both are odorless.

As a result of these findings the formula of a superior cattle spray was developed. This spray was placed upon the market by Stanco Incorporated under the name of "Molac."